

## ELECTROCHEMICAL REDUCTION OF METAL OXIDES

The present invention relates to electrochemical reduction of metal oxides.

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The present invention relates particularly to continuous and semi-continuous electrochemical reduction of metal oxides in the form of powder to produce metal having a low oxygen concentration, typically no more than 0.2% by weight.

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The present invention was made during the course of an on-going research project on electrochemical reduction of metal oxides being carried out by the applicant. The research project has focussed on the reduction of titania ( $\text{TiO}_2$ ).

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During the course of the research project the applicant carried out experimental work on the reduction of titania using electrolytic cells that included a pool of molten  $\text{CaCl}_2$ -based electrolyte, an anode formed from graphite, and a range of cathodes.

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The  $\text{CaCl}_2$ -based electrolyte was a commercially available source of  $\text{CaCl}_2$ , namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of  $\text{CaO}$ .

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The applicant operated the electrolytic cells at a potential above the decomposition potential of  $\text{CaO}$  and below the decomposition potential of  $\text{CaCl}_2$ .

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The applicant found that at these potentials the cell could electrochemically reduce titania to titanium with low concentrations of oxygen, ie concentrations less than 0.2 wt.%.

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The applicant operated the electrolytic cells on a batch basis with titania in the form of pellets and larger solid blocks in the early part of the work and titania powder in the later part of the work. The  
5 applicant also operated the electrolytic cells on a batch basis with other metal oxides.

Whilst the research work established that it is possible to electrochemically reduce titania (and other  
10 metal oxides) to metals having low concentrations of oxygen in such electrolytic cells, the applicant has realised that there are significant practical difficulties operating the electrolytic cells commercially on a batch basis.

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In the course of considering the results of the research work and possible commercialisation of the technology, the applicant realised that it was possible that commercial production could be achieved by operating  
20 an electrolytic cell on a continuous or semi-continuous basis with metal oxide powders and pellets being transported through the cell in a controlled manner and being discharged in a reduced form from the cell.

25 International application PCT/AU2003/001657, which claims priority from Australian provisional application 2002953282 lodged on 12 December 2002, in the name of the applicant describes this invention in broad terms as a process for electrochemically reducing a metal  
30 oxide, such as titania, in a solid state in an electrolytic cell that includes a bath of molten electrolyte, a cathode, and an anode, which process includes the steps of: (a) applying a cell potential across the anode and the cathode that is capable of  
35 electrochemically reducing metal oxide supplied to the molten electrolyte bath, (b) continuously or semi-continuously feeding the metal oxide in powder and/or

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pellet form into the molten electrolyte bath, (c) transporting the powders and/or pellets along a path within the molten electrolyte bath and reducing the metal oxide as the metal oxide powders and/or pellets move along the path, and (d) continuously or semi-continuously removing reduced metal oxide powders and/or pellets from the molten electrolyte bath.

The International application defines the term "powder and/or pellet form" as meaning particles having a particle size of 3.5 mm or less. The upper end of this particle size range covers particles that are usually described as pellets.

The term "powder" and "pellets" as used herein is understood to mean particles that are less than 5 mm in a major dimension.

The term "powder" and "pellets" as used herein is not intended to limit the scope of patent protection to a particular procedure for producing the particles.

The term "semi-continuously" is understood in the International application and herein to mean that the process includes: (a) periods during which metal oxide powders and/or pellets are supplied to the cell and periods during which there is no such supply of metal oxide powders and/or pellets to the cell, and (b) periods during which reduced material is removed from the cell and periods during which there is no such removal of reduced material from the cell.

The overall intention of the use of the terms "continuously" and "semi-continuously" in the International application and herein is to describe cell operation other than on a batch basis.

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In this context, the term "batch" is understood in the International application and herein to include situations in which metal oxide is continuously supplied to a cell and reduced metal builds up in the cell until  
5 the end of a cell cycle, such as disclosed in International application WO 01/62996 in the name of The Secretary of State for Defence.

After making the initial invention described  
10 above, the applicant carried out further research into the possibility of commercial production based on operating an electrolytic cell on a continuous or semi-continuous basis.

The applicant realised that a commercial  
15 production cell should include a cell cathode in the form of a member, such as a plate, having an upper surface for supporting metal oxides in pellet form, as described herein, that is horizontally disposed or slightly inclined  
20 and has a forward end and a rearward end and is immersed in the electrolyte bath and is supported for movement, preferably in forward and rearward directions, so as to cause metal oxide pellets to move toward the forward end of the cathode.

25 The applicant proposed that, with this arrangement, in use, metal oxides in powder and/or pellet form could be supplied onto the upper surface of the cathode, preferably near the rearward end thereof, and  
30 moved forward by the movement of the cathode and fall off the upper surface at the forward end of the cathode and ultimately be removed from the cell. With this arrangement, the metal oxides would be reduced as the metal oxides moved over the upper surface.

35 International application PCT/AU2004/000809, which claims priority from Australian provisional

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application 2003903150 lodged on 20 June 2003, in the name of the applicant describes this so-called "shaker table" cathode invention in broad terms.

5           The applicant has carried out further research and development work on the "shaker table" invention and has now designed a particular electrolytic cell in accordance with the invention. The invention of the particular electrolytic cell design is the subject of this  
10 patent specification.

          The particular electrolytic cell design of the present invention is characterised by multiple anodes and by support structures that separately support the "shaker  
15 table" cathode and the anodes from above the cell, and preferably with the anode support structure enabling adjustment of the spacing of the anodes above the upper surface of the "shaker table" cathode.

20           According to the present invention there is provided an electrolytic cell for electrochemically reducing metal oxide powders and/or pellets (as described herein), which electrolytic cell includes (a) a bath of a molten electrolyte, (b) a cathode in the form of a member,  
25 such as a plate, having an upper surface for supporting metal oxide powders and/or pellets that is horizontally disposed or slightly inclined and has a forward end and a rearward end and is immersed in the electrolyte bath, (c) a cathode support means for supporting the cathode from  
30 above the electrolyte bath and for moving the cathode in the cell so as to cause metal oxide powders and/or pellets on the upper surface of the cathode to move toward the forward end of the cathode while in contact with molten electrolyte whereby electrochemical reduction of the metal  
35 oxide can occur as the powders and/or pellets move toward the forward end, (d) a plurality of anodes extending into the electrolyte bath, (e) an anode support means for

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supporting the anodes from above the electrolyte bath, (f) a means for applying a potential across the anodes and the cathode, (g) a means for supplying metal oxide powders and/or pellets to the electrolyte bath so that the metal  
5 oxide powders and/or pellets can deposit onto the upper surface of the cathode, and (h) a means for removing at least partially electrochemically reduced metal oxides from the electrolyte bath.

10                    Preferably the anodes are arranged in pairs above the upper surface of the cathode.

                    Preferably there are a plurality of the pairs along the length of the upper surface of the cathode.

15                    Preferably each anode is in the form of a block of a suitable anode material, such as graphite, mounted on the end of a rod.

20                    The term "rod" is used herein in a general sense and includes any elongate member, such as a bar, that is suitable as a support member for an anode block.

                    Preferably the anode support means includes a  
25 fixed structure and a means for holding the anode rods to the structure above the electrolyte bath.

                    Preferably the means for holding the anode rods enables adjustment of the anode blocks vertically upwardly  
30 or downwardly so that the spacing of the ends of the anode blocks above the upper surface of the cathode can be varied.

                    Preferably the cathode support means includes:

35                    (a) a plurality of cathode support members, such as rods, extending upwardly from the

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cathode,

(b) a fixed structure,

- 5 (c) a movable structure supported by the fixed structure and movable with respect to the fixed structure, the movable structure including a means for holding the cathode support members so that the cathode is  
10 immersed in the electrolyte bath, and
- (d) a means coupled to the movable structure for moving the movable structure to thereby move the cathode in the cell so as to cause  
15 metal oxide powders and/or pellets on the upper surface of the cathode to move toward the forward end of the cathode.

20 Preferably the fixed structure of the anode support means is mounted to the fixed structure of the cathode support means.

25 Preferably the means for holding the cathode support members allows adjustment of the position of the cathode vertically upwardly or downwardly within the electrolyte bath.

30 Preferably the cathode support means is adapted to move the cathode in the cell to cause metal oxide powders and/or pellets on the upper surface of the cathode member to move over the upper surface of the cathode in forward and rearward directions.

35 Preferably the cathode is formed to cause metal oxide powders and/or pellets to move on the upper surface of the cathode toward the forward end of the cathode as a packed mono-layer of powders and/or pellets.

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For example, the cathode may be formed with an upstanding lip at the forward end that causes powders and/or pellets to build-up behind the lip. Alternatively, 5 or in addition, the upper surface of the cathode may be formed with a series of transversely extending grooves that promote close packing of the powders and/or pellets.

Preferably the means for applying an electrical 10 potential across the anode and the cathode includes an electrical circuit in which a power source is connected to a forward end of the cathode. The applicant has found that this arrangement results in substantial reduction of titania powders and/or pellets within a short distance 15 from the forward end of the cell.

Preferably the cathode support members extend upwardly from the opposed sides of the cathode.

20 Preferably the means for applying a potential across the anodes and the cathode includes (a) a power source and (b) an electrical circuit that electrically interconnects the power source, the anodes, and the cathode.

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Preferably the electrical circuit includes the cathode support members.

30 Preferably the size and/or the positions of the cathode support members is selected having regard to the requirements of (a) supporting the cathode in a stable manner within the electrolytic cell and (b) supplying a pre-selected current distribution to the cathode.

35 Preferably the cell includes a means for treating gases released from the cell.



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The gas treatment means may include a means for removing any one or more of carbon monoxide, carbon dioxide, chlorine-containing gases, and phosgene from the gases.

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The gas treatment means may also include a means for combusting carbon monoxide gas in the gases.

10 In a situation in which the metal oxide is titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents.

15 Preferably the particle size of the powders and/or pellets is in the range of 1-4 mm.

Typically, the particle size of the pellets is in the range of 1-3 mm.

20 According to the present invention there is also provided a process for electrochemically reducing metal oxide pellets, such as titania pellets, in the above-described electrolytic cell that includes the steps of:  
25 (a) applying a cell potential across the anodes and the cathode that is capable of electrochemically reducing metal oxide supplied to the molten electrolyte bath, (b) continuously or semi-continuously feeding metal oxide powders and/or pellets into the molten electrolyte bath so that the powders and/or pellets deposit on an upper  
30 surface of the cathode, (c) causing metal oxide powders and/or pellets to move over the upper surface of the cathode toward the forward end of the cathode while in contact with molten electrolyte whereby electrochemical reduction of the metal oxide occurs as the powders and/or  
35 pellets move toward the forward end, and (d) continuously or semi-continuously removing at least partially electrochemically reduced metal oxide powders and/or

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pellets from the molten electrolyte bath.

Preferably step (b) includes feeding the metal oxide powders and/or pellets into the molten electrolyte bath so that the powders and/or pellets form a mono-layer on an upper surface of the cathode.

In use, the metal oxide powders and/or pellets may be deposited on the upper surface of the cathode in a pile of powders and/or pellets and may be shaken out into a mono-layer as the cathode moves the pellets towards the forward end of the cathode.

Preferably step (c) includes causing metal oxide powders and/or pellets to move on the upper surface of the cathode toward the forward end of the cathode as a packed mono-layer of powders and/or pellets.

The packed mono-layer may be produced by forming the cathode appropriately. For example, the cathode may be formed with an upstanding lip at the forward end that causes powders and/or pellets to build-up behind the lip. Alternatively, or in addition, the cathode may be formed with a series of transversely extending grooves that promote close packing of the powders and/or pellets.

Preferably step (c) includes selectively moving the cathode so as to cause metal oxide powders and/or pellets on the upper surface of the cathode to move toward the forward end of the cathode.

There is a wide range of options for moving the cathode to cause forward movement of powders and/or pellets on the upper surface of the cathode. The applicant has found that it is preferable to move the cathode in forward and rearward directions. The applicant has found that one option that can achieve controlled forward

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movement of powders and/or pellets includes moving the cathode in a repeated sequence that comprises a short period of oscillating motion in the forward and rearward directions and a short rest period. The applicant has  
5 found that this sequence can cause powders and/or pellets on the upper surface of the cathode to move over the upper surface in a controlled series of short steps from the rearward end to the forward end of the cell.

10 Moreover, the present invention is not confined to operating a cell under constant operating conditions and extends to situations in which the operating parameters, such as the cathode movement, are varied during the operating campaign of the cell.

15 Preferably step (c) includes moving the cathode so as to cause powders and/or pellets across the width of the cathode to move at the same rate so that the powders and/or pellets have substantially the same residence time  
20 within the bath.

Preferably the process electrochemically reduces the metal oxide to metal having a concentration of oxygen that is no more than 0.3% by weight.

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More preferably the concentration of oxygen is no more than 0.2% by weight.

The process may be a single or multiple stage  
30 process involving one or more than one electrolytic cell.

In the case of a multiple stage process involving more than one electrolytic cell, the process may include successively passing reduced and partially reduced metal  
35 oxides from a first electrolytic cell through one or more than one downstream electrolytic cell and continuing reduction of the metal oxides in these cells.

In a situation in which the cathode is in the form of a plate, another option for a multiple stage process includes successively passing reduced and  
5 partially reduced metal oxides from one cathode plate to another cathode plate or a succession of cathode plates within one electrolytic cell.

Another option for a multiple stage process  
10 includes recirculating reduced and partially reduced metal oxides through the same electrolytic cell.

Preferably the process includes washing pellets that are removed from the cell to separate electrolyte  
15 that is carried from the cell with the powders and/or pellets.

The process inevitably results in a loss of electrolyte from the cell and, therefore make-up  
20 electrolyte will be required for the cell.

The make-up electrolyte may be obtained by recovering electrolyte that is washed from the powders and/or pellets and recycling the electrolyte to the cell.  
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Alternatively, or in addition, the process may include supplying fresh make-up electrolyte to the cell.

Preferably the process includes maintaining the  
30 cell temperature below the vaporisation and/or decomposition temperatures of the electrolyte.

Preferably the process includes applying a cell potential above a decomposition potential of at least one  
35 constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

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In a situation in which the metal oxide is titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents.

In such a situation it is preferred that the process includes maintaining the cell potential above the decomposition potential for  $\text{CaO}$ .

The present invention is described further by way of example with reference to the accompanying drawings of which:

Figure 1 is a schematic diagram that illustrates one embodiment of an electrochemical process and an electrolytic cell in accordance with the present invention;

Figure 2 is a perspective view of the electrolytic cell shown in Figure 1, with the cathode support rods removed to clarify the Figure;

Figure 3 a vertical section through the electrolytic cell shown in Figures 1 and 2;

Figure 4 is the vertical section shown in Figure 3 with the top cover and the anodes and the anode support structure removed to illustrate the cathode and the cathode support structure more clearly; and

Figure 5 is the vertical section shown in Figure 3 with the top cover and the cathode and the cathode support structure removed to illustrate the anodes and the anode support structure more clearly.

The following description is in the context of

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electrochemically reducing titania pellets to titanium metal having an oxygen concentration of less than 0.3 wt.%. However, it is noted that the present invention is not confined to this metal oxide and extends to other metal oxides. It is also noted that the present invention is not confined to electrochemical reduction of pellets and also extends to electrochemical reduction of powders as described herein.

The electrolytic cell 1 shown in the drawings is an enclosed chamber, although not completely sealed, that is rectangular in top plan and has a base wall 3, a pair of opposed end walls 5, a pair of opposed side walls 7, and a top cover 9.

The cell includes a series of inlets for titania pellets in the top cover 9 near the left hand end of the cell as viewed in Figures 1, 3, 4, and 5 and near the right hand end of the cell as viewed in Figure 2. This end of the cell is hereinafter referred to as "the rearward end" of the cell. The inlets are identified by the numeral 11 in Figure 2.

The pellets are formed in a "green" state in a pan pelletiser 51 and are then sintered in a sintering furnace 53 and thereafter are stored in a storage bin 55. Typically, the pellets have a size range of 1-4 mm. Pellets from the storage bin 55 are supplied via a vibratory feeder 57 to the cell inlets 11.

The cell further includes an outlet 13 for titanium metal pellets in the base wall 3 near the right hand end of the cell as viewed in Figures 1, 3, 4, and 5 and near the right hand end of the cell as viewed in Figure 2. This end of the cell is hereinafter referred to as "the forward end" of the cell. The outlet 13 is in the form of a sump defined by downwardly converging sides 15 and an

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upwardly inclined auger 35 or other suitable means arranged to receive titanium pellets from a lower end of the sump and to transport the pellets away from the cell.

5           The cell contains a bath 21 of molten electrolyte. The preferred electrolyte is  $\text{CaCl}_2$  with at least some  $\text{CaO}$ .

10           The cell further includes a cathode 25 in the form of a plate or other suitable member that is immersed in the bath 21 and is positioned a short distance above the base wall 3. The cathode plate 25 is supported in the cell by a support structure described hereinafter so that the upper surface of the cathode plate 25 is horizontal or  
15           slightly inclined downwardly from the rearward end to the forward end of the cell. The length and width dimensions of the cathode plate 25 are selected to be as large as possible to fit conveniently within the cell. The cathode plate 25 is supported to move in the forward and rearward  
20           directions in an oscillating motion as described hereinafter.

          The cathode support structure includes a fixed support structure of vertical posts 71 and a pair of  
25           horizontal cross members 73 mounted on the posts. In addition, the support structure includes a carriage 75 that is arranged for forward and rearward horizontal sliding movement on the cross members 73 and an hydraulic actuator 77 that is mounted on the cross members 73 and is  
30           coupled to the carriage 75 to move the carriage. The support structure also includes 6 screw jacks 81 mounted to the carriage 75 and 6 elongate cathode support members 79 that are connected at lower ends to the opposed sides of the cathode plate 25 and are supported at upper ends by  
35           the screw jacks 81. The support members 79 are arranged in pairs on opposite sides of the cathode plate 25. Thus, there are 3 support members 79 on each side of the cathode

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plate 25. The screw jacks 81 hold the support members 79, and thereby the cathode plate 25, for controlled movement downwardly into or upwardly from the electrolyte bath 21 to enable height adjustment of the cathode plate within the electrolyte bath 21. In addition, as will be apparent from the above, sliding movement of the carriage 75 in forward and rearward directions via operation of the actuator 77 causes horizontal sliding movement of the cathode plate 25 in the electrolyte bath 21. The top cover 9 of the cell includes openings 93 (see Figures 2 and 3) for the support members 79 and the openings are sufficiently large to accommodate such sliding movement of the carriage 75 and therefore the support members 79.

The cell further includes 6 anodes generally identified by the numeral 19 that extend into the bath 21. The anodes 19 include graphite blocks 23 mounted to the ends of rods or other suitable support members 27. The anode blocks 19 include lengthwise extending slots 91 (see Figure 2) to allow gas that evolves in the electrolyte bath 21 to escape from the cell. The anodes 19 are arranged in pairs and the size of the anode blocks 23 is selected so that the anodes are positioned directly above substantially the whole of the upper surface of the cathode plate 25. The anodes 19 are supported by a support structure described hereinafter so that the anode blocks 23 can be progressively lowered into the bath 21 as lower sections of the anode graphite are consumed by cell reactions at the anodes. The top cover 9 of the cell includes openings 95 (see Figures 2 and 3) for the support members 27.

The anode support structure includes a fixed support structure of vertical posts 63 and an assembly of horizontal cross members 65 mounted on the posts. The support structure also includes 6 screw jacks 67 mounted to a pair of parallel cross members 65 and holding the 6



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anodes 19. Specifically, the screw jacks 67 hold the anode support members 27, and thereby the anode blocks 23, for controlled movement downwardly into or upwardly from the electrolyte bath 21.

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The applicant has found that movement of the cathode plate 25 in a repeated sequence that comprises a short period of forward and backward, ie oscillating, motion and a short rest period can cause pellets on the upper surface of the cathode plate 25 to move over the upper surface in a series of short steps from the rearward end to the forward end of the cell.

Moreover, the applicant has found that the above-described type of motion can cause pellets across the width of the cathode plate 25 to move at a constant rate so that the pellets have substantially the same residence time within the bath 21.

More particularly, the cell is arranged so that, in use, titania pellets supplied to the cell via the inlets 11 fall downwardly onto the upper surface of the cathode plate 25 near the rearward end of the cell and are caused to move forwardly over the upper surface of the cathode plate 25 and fall off the forward end of the cathode plate 25 into the outlet 13. More particularly, the cell is arranged so that, in use, the pellets move forwardly over the upper surface of the cathode plate 25 as a closely packed mono-layer. In order to achieve close packing of the pellets, the cathode plate 25 includes an upstanding lip (not shown) at the forward end thereof that causes pellets to build-up behind the lip along the length of the cathode plate 25.

The applicant has found that it is preferable that the titania pellets be substantially round since it is possible to cause these pellets to move over the upper

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surface of the cathode plate 25 in a more predictable manner than is possible with more angular pellets.

5 In addition, the applicant has found that it is undesirable that the pellets "stick" to the upper surface of the cathode to an extent that inhibits forward movement of the pellets and that the pellets "stick" together. These considerations support the preference for round pellets. It is relevant to note that oscillating movement  
10 of the cathode plate 25 minimises sticking of pellets.

The applicant has also found that the size and weight of the pellets should be selected so that the pellets settle quite quickly onto the upper surface of the  
15 cathode plate 25 and do not become suspended in the electrolyte in the molten bath 21.

In overall terms, it is preferable to select the smallest possible pellet size that can move over the  
20 cathode plate 25 in an efficient manner, i.e. without sticking to the cathode, in order to optimise mass throughput of the cell.

The cell further includes a power source 31 for  
25 applying a potential across the anode block 23 and the cathode plate 25 and an electrical circuit (that includes the above-described cathode support members 79) electrically interconnects the power source 31, the anodes 23, and the cathode. The size and/or the positions of the  
30 cathode support members 79 is selected to supply a preselected current distribution to the cathode plate 25 to optimise electrochemical reduction of titania pellets on the cathode plate 25. Depending on the circumstances, there may be a range of current distributions required in  
35 the operation of the cell.

In use of the cell, titania pellets are supplied

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to the upper surface of the cathode plate 25 at the rearward end of the cell so as to form a mono-layer of pellets on the cathode plate 25 and the cathode is moved as described above and causes the pellets to step forward over the surface of the plate to the forward end of the cell and ultimately fall from the forward end of the cathode. The pellets are progressively electrochemically reduced in the cell as the pellets are moved over the surface of the cathode plate 25. The operating parameters of the cathode plate 25 are selected so that the pellets have sufficient residence time in the cell to achieve a required level of reduction of the titania pellets. Typically, 2-4 mm titania pellets require 4 hours residence time to be reduced to titanium with a concentration of 0.3 wt% oxygen at a cell operating voltage of 3 V.

The applicant has found that the above-described arrangement results in substantial reduction of titania pellets within a short distance from the forward end of the cell.

The applicant has found that there are a number of factors that have an impact on the overall operation of the cell. Some of these factors, namely pellet size and shape and motion of the cathode plate 25, are discussed above. Another relevant factor is the exposed surface areas of the upper surface of the cathode plate 25 and the anode block 23. On the basis of work to date, the applicant believes that larger rather than smaller cathodes 25 in relation to the exposed surface area of the anode blocks 23 is preferable. In other words, the applicant believes that a larger rather than a smaller anodic current density is preferable.

In use of the cell, the anode blocks 23 are progressively consumed by a reaction between carbon in the

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anode block 23 and  $O^{--}$  anions generated at the cathode plate 25, and the reaction occurs predominantly at the lower edges of the anode blocks 23.

5           The distances between the upper surface of the cathode plate 25 and the lower edges of the anode blocks 23 are maintained as required.

10           Preferably the distance between the upper surface of the cathode plate 25 and the lower edges of the anode block 23 is selected so that there is sufficient resistance heating generated to maintain the bath 21 at a required operating temperature.

15           Preferably the cell is operated at a potential that is above the decomposition potential of. Depending on the circumstances, the potential may be as high as 4-5V. In accordance with the above-described mechanism, operating above the decomposition potential of CaO  
20 facilitates deposition of Ca metal on the cathode plate 25 due to the presence of  $Ca^{++}$  cations and migration of  $O^{--}$  anions to the anode block 23 as a consequence of the applied field and reaction of the  $O^{--}$  anions with carbon of the anode block 23 to generate carbon monoxide and carbon  
25 dioxide and release electrons. In addition, in accordance with the above-described mechanism, the deposition of Ca metal results in chemical reduction of titania via the mechanism described above and generates  $O^{--}$  anions that migrate to the anode block 23 as a consequence of the  
30 applied field and further release of electrons. Operating the cell below the decomposition potential of  $CaCl_2$  minimises evolution of chlorine gas, and is an advantage on this basis.

35           As is indicated above, the operation of the cell generates carbon monoxide and carbon dioxide and potentially chlorine-containing gases at the anode blocks

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23 and it is important to remove these gases from the cell. The cell further includes an off-gas outlet 41 in the top cover 9 of the cell and a gas treatment unit 43 that treats the off-gases before releasing the treated  
5 gases to atmosphere. The gas treatment includes removing carbon dioxide and any chlorine gases and may also include combusting carbon monoxide to generate heat for the process.

10 Titanium pellets, together with electrolyte that is retained in the pores of the titanium pellets, are removed from the cell continuously or semi-continuously at the outlet 13. The discharged material is transported via the auger 35 to a water spray chamber 37 and quenched to a  
15 temperature that is below the solidification temperature of the electrolyte, whereby the electrolyte blocks direct exposure of the metal and thereby restricts oxidation of the metal. The discharged material is then washed to separate the retained electrolyte from the metal powder.  
20 The metal powder is thereafter processed as required to produce end products.

The above-described cell and process are an efficient and an effective means of continuously and semi-  
25 continuously electrochemically reducing metal oxides in the form of pellets to produce metal having a low oxygen concentration

Specifically, the electrolytic cell shown in the  
30 drawing is one example only of a large number of possible cell configurations that are within the scope of the present invention.